19.1 Ketones and Aldehydes

• Both functional groups possess the carbonyl group

• Important in both biology and industry

Simplest aldehyde
used as a preservative

Simplest ketone
used mainly as a solvent

Formaldehyde
Acetone

Copyright © 2017 John Wiley & Sons, Inc. All rights reserved.
19.1 Ketones and Aldehydes

Vanillin (Vanilla flavor)
Cinnamaldehyde (Cinnamon flavor)
(R)-Carvone (Spearmint flavor)
Benzaldehyde (Almond flavor)

Progesterone
Testosterone
19.2 Nomenclature

- Four discrete steps to naming an aldehyde or ketone
- Same procedure as with alkanes, alcohols, etc...

1. Identify and name the parent chain
2. Identify the name of the substituents (side groups)
3. Assign a locant (number) to each substituents
4. Assemble the name alphabetically
1. Identify and name the parent chain
   
   - For aldehydes, replace the “-e” ending with an “-al”

   ![Butane](image1)  
   ![Butanal](image2)

   - the parent chain must include the carbonyl carbon

   ![Parent = Octane](image3)  
   ![Parent = Hexanal](image4)

   The parent must include this carbon atom.
19.2 Nomenclature

1. Identify and name the parent chain

   - The aldehydic carbon is assigned number 1:
1. Identify and name the parent chain

- For ketones, replace the “-e” ending with an “-one”

- The parent chain must include the C=O group
- the C=O carbon is given the lowest #, and can be expressed before the parent name or before the suffix
The configuration of a chiral center is indicated at the beginning of the name.

- **Aldehyde next to a ring is named as a carbaldehyde.**

  - (R)-2-Chloro-3-phenylpropanal

  - Cyclohexane carbaldehyde
19.2 Nomenclature

- IUPAC also recognizes the following common names as parent names:
  - Formaldehyde
  - Acetaldehyde
  - Benzaldehyde

- Practice with SkillBuilder 19.1
19.3 Preparing Aldehydes and Ketones

- Summary of aldehyde preparation (review)

<table>
<thead>
<tr>
<th>REACTION</th>
<th>SECTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozonolysis of Alkenes</td>
<td>8.12</td>
</tr>
</tbody>
</table>

H  
R  
\[ \text{H} \quad \text{H} \quad \text{1) O}_3 \quad \text{H} \quad \text{O} \quad \text{O} \quad \text{H} \quad \text{R} \quad \text{DMS} \quad \text{R} \quad \text{R} \]

Ozonolysis will cleave a C=\( \equiv \)C double bond. If either carbon atom bears a hydrogen atom, an aldehyde will be formed.
19.3 Preparing Aldehydes and Ketones

- Summary of aldehyde preparation (review)

<table>
<thead>
<tr>
<th>REACTION</th>
<th>SECTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroboration-Oxidation of Terminal Alkynes</td>
<td>9.7</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{R} & \quad \text{1) } R_2\text{B–H} \\
& \quad \text{2) } \text{H}_2\text{O}_2, \text{NaOH} \\
\text{H} & \quad \text{R} \\
\text{O} & \quad \text{H}
\end{align*}
\]

Hydroboration-oxidation results in an *anti*-Markovnikov addition of water across a \( \pi \) bond, followed by tautomerization of the resulting enol to form an aldehyde.
19.4 Nucleophilic Addition Reactions

- The carbonyl carbon is electrophilic; this is derived from resonance effects and inductive effects.
19.4 Nucleophilic Addition Reactions

- The carbonyl carbon is attacked by nucleophiles, forming a new $\sigma$ bond in exchange for the C=O $\pi$ bond, and becoming a tetrahedral center:
19.4 Nucleophilic Addition Reactions

• Aldehydes are generally more reactive towards nucleophiles than ketones:

1. **Steric effects** - aldehydes are less sterically hindered

2. **Electronic effects** - aldehyde has a larger $\delta^+$ on the carbonyl carbon:

- A ketone has **two** electron-donating alkyl groups that stabilize the partial positive charge
- An aldehyde has **only one** electron-donating alkyl group that stabilizes the partial positive charge
19.4 Nucleophilic Addition Reactions

- Under **basic conditions**, all nucleophiles react with carbonyls by the **same general mechanism**:

**MECHANISM 19.1 NUCLEOPHILIC ADDITION UNDER BASIC CONDITIONS**

- Nucleophile attacks, forming a **negatively charged intermediate**, which is protonated upon acidic workup.
19.4 Nucleophilic Addition Reactions

- Aldehydes/ketones react with a variety of weaker nucleophiles, under **acidic conditions**, by the same general mechanism:

**MECHANISM 19.2 NUCLEOPHILIC ADDITION UNDER ACIDIC CONDITIONS**

- The carbonyl group is first protonated, rendering it even more electrophilic.
- The protonated carbonyl group is then attacked by a nucleophile.

- The carbonyl is protonated to form a **positively charged intermediate**, which can be attacked by a weak nucleophile.
19.4 Nucleophilic Addition Reactions

- Acidic conditions are required in order for a weak nucleophile to attack a carbonyl carbon:

\[
\text{Acidic conditions: } \overset{\text{H}}{\text{C}} = \overset{\text{O}}{\text{H}} \rightarrow \overset{\text{O}}{\text{H}} \left(\overset{\text{+}}{\text{C}}\right)
\]

- Protonation of the carbonyl makes it a better electrophile.
19.4 Nucleophilic Addition Reactions

- When a nucleophile attacks a carbonyl group, the equilibrium depends on the ability of the nucleophile to function as a leaving group.
- **Example:**

  \[
  \text{R} \quad \text{R} \quad \text{O} \quad + \quad \text{HCl} \quad \rightleftharpoons \quad \text{R} \quad \text{R} \quad \text{HO} \quad \text{Cl}
  \]

  Favored at equilibrium

- Since the nucleophile, Cl\(^-\), is also a good leaving group, equilibrium favors the starting ketone.
19.4 Nucleophilic Addition Reactions

- We will cover the following nucleophiles and their reaction with ketones and aldehydes:

- Practice with Conceptual Checkpoint 19.6
19.5 Oxygen Nucleophiles

- In the presence of water, a ketone/aldehyde is in equilibrium with its hydrate:

\[
\text{ketone/aldehyde} + \text{H}_2\text{O} \rightleftharpoons \text{hydrate}
\]

- Equilibrium generally does not favor the formation of the hydrate (except for very simple aldehydes)

- The rate of reaction is slow unless acidic or basic conditions are used
19.5 Oxygen Nucleophiles

• Under basic conditions, OH\(^-\) is the nucleophile:

**MECHANISM 19.3  BASE-CATALYZED HYDRATION**

Nucleophilic attack

The carbonyl group is attacked by hydroxide, forming an anionic intermediate

Proton transfer

The anionic intermediate is protonated by water to form the hydrate
19.5 Oxygen Nucleophiles

- Under acidic conditions, the carbonyl is protonated, and H₂O is the nucleophile:

  - The carbonyl group is protonated, rendering it more electrophilic.
  - The protonated carbonyl group is attacked by water, forming an oxonium intermediate.
  - The oxonium intermediate is deprotonated by water to form the hydrate.

- Practice with Conceptual Checkpoint 19.7
19.5 Oxygen Nucleophiles

- KEEP THE FOLLOWING IN MIND WHEN DRAWING MECHANISMS:

- Under acidic conditions, a mechanism will only be reasonable if it avoids the use or formation of strong bases
  - A strong base cannot exist in an acidic environment.

- Under basic conditions, a mechanism will only be reasonable if it avoids the use of formation of strong acids
  - A strong acid cannot exist in a basic environment.
19.5 Oxygen Nucleophiles

- Alcohols can attack ketones/aldehydes:

\[
\text{O} + 2 \text{ROH} \xrightleftharpoons{[H^+]} \text{RO OR} \xrightarrow{} \text{Acetal} + \text{H}_2\text{O}
\]

- Under acidic conditions, 1 ketone/aldehyde reacts with 2 alcohols to form an acetal.

Commonly used acid catalysts for acetal formation:

- p-Toluenesulfonic acid (TsOH)
- Sulfuric acid
19.5 Oxygen Nucleophiles

The carbonyl group is protonated, rendering it more electrophilic.

The alcohol attacks the protonated carbonyl to generate an oxonium intermediate.

The oxonium intermediate is deprotonated to form a hemiacetal.

The OH group is protonated, thereby converting it into an excellent leaving group.

Loss of a leaving group.

Water leaves to regenerate the C=O double bond.

Acetal

The oxonium intermediate is deprotonated, generating an acetal.

The second molecule of the alcohol attacks the C=O double bond to generate another oxonium intermediate.
19.5 Oxygen Nucleophiles

- Acetal formation is an equilibrating process
  - For most simple aldehydes, the acetal is favored at equilibrium
  - For most ketones, the acetal is *not* favored at equilibrium
19.5 Oxygen Nucleophiles

- If a diol is used, then both equivalents of alcohol come from the same compound, and a cyclic acetal is formed.

- Practice drawing the mechanism of acetal formation with SkillBuilder 19.2.
Acetal formation is reversible, and can be controlled by adding/removing water:

- **To favor acetal formation, water is removed** from the reaction.
- **To convert an acetal back into the ketone/aldehyde, water is added** to the acetal, with H+ catalyst:

In this way, acetals can be used as protecting groups for ketones/aldehydes.
19.5 Oxygen Nucleophiles

- Consider how the following synthesis could be accomplished:

\[ \text{ester} \rightarrow \text{alcohol} \]

- We need to convert an ester to 1° alcohol, which requires LAH, while leaving the ketone unchanged.

- **problem**: Using LAH would reduce the ketone as well
- **solution**: use a protecting group for the ketone
19.5 Oxygen Nucleophiles

• First, protect the ketone as a cyclic acetal:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{OR} & \quad \text{OR} \\
\text{HO} & \quad \text{OH} \\
\text{[H}^+\text{], H}_2\text{O} & \quad \text{H}_2\text{O} \\
\end{align*}
\]

• Then we can reduce the ester, and deprotect the ketone

• Overall:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{OR} & \quad \text{OR} \\
\text{1)} [\text{H}^+, \text{HO}OH, \text{H}_2\text{O}] & \quad \text{H}_2\text{O} \\
\text{2)} \text{LiAlH}_4 & \\
\text{3)} \text{H}_3\text{O}^+ & \\
\end{align*}
\]

• Practice with Conceptual Checkpoint 19.10-19.11
19.5 Oxygen Nucleophiles

- A **hemiacetal** is the intermediate formed in the conversion of a ketone/aldehyde to an acetal.
- The are generally difficult to isolate, as equilibrium either favors the aldehyde/ketone or the acetal, based on conditions used:

\[
\text{Ketone} + 2 \text{ROH} \rightleftharpoons \text{Hemiacetal} \rightleftharpoons \text{Acetal} + \text{H}_2\text{O}
\]

- Favored by the equilibrium
- Difficult to isolate
- Favored when water is removed

- However, **cyclic hemiacetals** can be usually be isolated.
19.5 Oxygen Nucleophiles

• A **cyclic hemiacetal** is possible when a compound contains both the carbonyl group and the hydroxy group:

![Cyclic hemiacetal](image)

- **Cyclic hemiacetals are important in carbohydrate chemistry:**

![Glucose](image)
19.6 Nitrogen Nucleophiles

- Under acidic conditions, **aldehyde/ketone** reacts with a **1° amine** to form an **imine**:

\[
\text{[H}^+] \quad \text{CH}_3\text{NH}_2 \quad \rightarrow \quad \text{Imine (C=N double bond)}
\]

- The reaction requires acidic conditions to work;
19.6 Nitrogen Nucleophiles

- Nucleophilic attack
  - The amine attacks the carbonyl group

- Proton transfer
  - The intermediate is protonated to remove the negative charge
  - Deprotonation gives a carbinolamine

- Proton transfer
  - Carbinolamine

- Proton transfer
  - The OH group is protonated thereby converting it into an excellent leaving group

- Proton transfer
  - Loss of a leaving group

- Imine
  - The intermediate is deprotonated to generate an imine

- Water leaves, forming a C≡N double bond
19.6 Nitrogen Nucleophiles

• Even though it is under acidic conditions, protonation of the carbonyl is not the first step of imine formation mechanism.

Amines are bases, and consume the H+ catalyst.

The ammonium ion is the acid catalyst for the reaction.

• The ammonium ion is not acidic enough to protonate an aldehyde or ketone, but it is acidic enough to transfer a proton to the negatively charged oxygen in the second step.
19.6 Nitrogen Nucleophiles

- For imine formation, the pH has to be right around 5, or the reaction is too slow.

lower pH = all the amines are protonated, none available to attack the carbonyl

higher pH = not enough acid to catalyze the reaction effectively

Practice with SkillBuilder 19.3
19.6 Nitrogen Nucleophiles

• Under acidic conditions, aldehyde/ketone reacts with a 2° amine to form an enamine:

![Chemical structure](image)

![Chemical structure](image)

• The reaction requires acidic conditions to work; the mechanism is identical to imine formation, except for the last step.
19.6 Nitrogen Nucleophiles

- **Nucleophilic attack**
  - The amine attacks the carbonyl group.

- **Proton transfer**
  - The intermediate is protonated to remove the negative charge.

- **Proton transfer**
  - Deprotonation gives a carbinolamine.

- **Carbinolamine**
  - The OH group is protonated, thereby converting it into an excellent leaving group.

- **Proton transfer**
  - The intermediate is deprotonated to generate an enamine.

- **Loss of a leaving group**
  - Water leaves and a C=N double bond forms.
19.6 Nitrogen Nucleophiles

- The reaction requires acidic conditions to work; the mechanism is identical to imine formation, except for the last step

- Practice with SkillBuilder 19.4
Wolff-Kishner reduction is a two-step synthesis, converting a ketone to an alkane:

1. First step is imine formation between the ketone and hydrazine (which is like a primary amine)

2. Second reaction is like an elimination
19.6 Nitrogen Nucleophiles

- Mechanism of 2\textsuperscript{nd} step of Wolff-Kishner reduction:

  - One of the protons is removed, forming a resonance-stabilized intermediate.
  - The intermediate is protonated.
  - Another proton is removed.
  - The carbanion is protonated, generating the product.
  - Nitrogen gas is expelled, generating a carbanion.

- Practice with Conceptual Checkpoint 19.22
19.6 Nitrogen Nucleophiles

• Note the many similarities between the acid catalyzed mechanisms we have discussed

• One thing to always note:

Under acidic conditions, reaction species should either be neutral or have a +1 formal charge
19.7 Hydrolysis of Acetals

• Acetals are hydrolyzed with aqueous acid to yield a ketone (or aldehyde) and two equivalents of alcohol:

• Simply the reverse of acetal formation:

\[ \text{Acetal} + \text{H}_2\text{O} \xrightarrow{[\text{H}^+]} \text{Ketone} + 2 \text{ROH} \]

• Acetals will only react with water under acidic conditions:

\[ \text{Acetal} \xrightarrow{\text{NaOH}} \text{No reaction} \]

Copyright © 2017 John Wiley & Sons, Inc. All rights reserved.

Klein, Organic Chemistry 3e
19.7 Hydrolysis of Acetals

The carbonyl group is protonated, rendering it more electrophilic.

A molecule of alcohol (ROH) is ejected as a leaving group.

Water functions as a nucleophile and attacks the powerful electrophile.

The hemiacetal is protonated, generating an excellent leaving group.

Water functions as a base and removes a proton, giving a hemicetal.
19.7 Hydrolysis of Imines and Enamines

- Hydrolysis of imines and enamines undergoes a very similar mechanism under acidic conditions.

\[
\begin{align*}
\text{N} & \quad \text{+ H}_2\text{O} \quad \xrightarrow{[\text{H}^+]} \quad \text{O} \quad \text{+ R} \text{N}\text{H}_2 \\
\text{R} & \quad \text{N} & \quad \text{+ H}_2\text{O} \quad \xrightarrow{[\text{H}^+]} \quad \text{O} \quad \text{+ R}_2\text{NH}
\end{align*}
\]

- The mechanism of hydrolysis for imines and enamines is simply the reverse of their mechanisms of formation.

- Practice with SkillBuilder 19.5
19.9 Hydrogen Nucleophiles

• Recall, aldehydes/ketones reduced to alcohols with a hydride reagent
• LiAlH$_4$ and NaBH$_4$ function as hydride delivery reagents:

These reductions are **carried out under basic conditions** (hydrides are strong nucleophiles)
19.9 Hydrogen Nucleophiles

- Basic conditions, so the first step of the mechanism is nucleophilic attack:

Nucleophilic attack

Lithium aluminum hydride (LiAlH₄) functions as a delivery agent of hydride ions (H⁻)

Proton transfer

The resulting alkoxide intermediate is protonated to form an alcohol
19.9 Hydrogen Nucleophiles

• Recall, reduction of an unsymmetrical ketone forms a new chiral center:

\[
\begin{align*}
\text{unsymmetrical ketone} & \\
\text{mixture of stereoisomers} & \\
\text{Racemic mixture} & \\
\end{align*}
\]

• Practice with Conceptual Checkpoint 19.28-19.29
19.10 Carbon Nucleophiles

- Recall, grignard reagents attack ketones/aldehydes to make an alcohol, with a new C-C bond:

\[
\text{O} \quad \xrightarrow{\text{1) CH}_3\text{MgBr}} \quad \text{H}_3\text{C}-\text{OH} \quad \xrightarrow{\text{2) H}_2\text{O}} \quad \text{O} \quad \xrightarrow{\text{1) CH}_3\text{MgBr}} \quad \text{OH} \quad \xrightarrow{\text{2) H}_2\text{O}} \quad \text{OH}
\]

- **Note:** either face of the carbonyl is attacked by the nucleophile, and a new chiral center may result.
Using Organometallic compounds (Chemistry of carbanions)

M = Na, K

explosive

Mg, Li

Versatile and useful

Pb, Sn, Hg, Tl

strong base (H-abstraction), strong nucleophiles
Preparation

\[ R - \text{Br} + 2 \text{Li} \rightarrow R - \text{Li} + \text{LiBr} \]

Ethers are the preferred solvents but:

Ethers are slowly attacked and decomposed
Grignard reagents: the most popular

\[ \text{R} \cdot \cdot \cdot \text{X} \rightarrow \text{R-Mg-X} \]

- possible with a great variety of R
- ethers as solvent are crucial to the success of the reaction

\[ \text{R-Mg-X} \leftrightarrow \text{R}_2\text{Mg} + \text{MgX}_2 \]
Grignard reagents: the most popular

\[ \text{Mg} \quad \cdot \cdot \cdot \]  \[ \text{R} \cdot \cdot \cdot \text{X} \rightarrow \text{R-Mg-X} \]

- possible with a great variety of R

- ethers as solvent are crucial to the success of the reaction

\[ \text{R-Mg-X} \quad \leftrightarrow \quad \text{R}_2\text{Mg} + \text{MgX}_2 \]
The strong polarity of the M-C bond and the consequent carbanionic character determines the reactivity:

1) superstrong base
Nucleophilic Addition (prep. of ROH)

Use acid hydrolysis to avoid precipitation of Mg(OH)$_2$
Formation of alcohols

Formaldehyde

\[ \text{R-MgX} \]

\[ \text{H} \quad \text{C} \quad \text{O} \]

\[ \text{H} \quad \text{C} \quad \text{O} \]

\[ \text{R-MgX} \]

\[ \text{H} \quad \text{C} \quad \text{OH} \]

\[ \text{H} \quad \text{C} \quad \text{OH} \]

\[ \text{R} \quad \text{C} \quad \text{OH} \]

\[ \text{R} \quad \text{C} \quad \text{OH} \]

Aldehyde

\[ \text{R-MgX} \]

\[ \text{R-MgX} \]

ketone

\[ \text{R} \quad \text{C} \quad \text{OH} \]

\[ \text{R} \quad \text{C} \quad \text{OH} \]

\[ \text{R} \quad \text{C} \quad \text{OH} \]

\[ \text{R} \quad \text{C} \quad \text{OH} \]
Reaction with both esters and acyl halides

Two identical groups
Planning a Grignard Synthesis

We can synthesize **ANY** alcohol
Restrictions

Incompatible with any function that can be deprotonated:

-\( \text{-OH, -NH}_2, -\text{NHR, -CO}_2\text{H, -SO}_3\text{H, -SH, -CC-H, aldehyde, ketone, esters, amide} \)
-\( \text{-NO}_2, -\text{CN, epoxide} \)

Grignard carbonatation to length the chain by one C atom
12. What is the product, A, that would be obtained from the following reaction sequence?

\[
\text{OH} \quad \xrightarrow{\text{PBr}_3} \quad \text{Li} \quad \xrightarrow{(\text{CH}_3)_2\text{C}=\text{O}} \quad \xrightarrow{\text{NH}_4\text{Cl}} \quad 10^\circ\text{C} \quad \text{A}
\]

Options:
- I
- II
- III
- IV
- V
9. What is the final product of the following reaction sequence?

\[ \text{CH}_3\text{I} \xrightarrow{\text{Mg, ether}} \text{organic product} \xrightarrow{(1) \text{CH}_3\text{CHCH}_2\text{CH}} \text{organic product} \xrightarrow{(2) \text{H}_3\text{O}^+} \text{product} \xrightarrow{\text{H}_2\text{CrO}_4, \text{acetone}} \text{final product} \]

A) \((\text{CH}_3)_2\text{CHCH}_2\text{CHOHCH}_3\)

B) \((\text{CH}_3)_2\text{CHCH}_2\text{COCH}_3\)

C) \((\text{CH}_3)_2\text{CHCCH}_2\text{CH}_3\)

D) \((\text{CH}_3)_2\text{CHCHOHCH}_2\text{CH}_3\)

E) \((\text{CH}_3)_2\text{CHCH}_2\text{CCH}_3\)
10. The product, B, of the following reaction,

\[
\text{CH}_3\text{CCH}_3 + \text{NaBD}_4 \rightarrow \text{A} \xrightarrow{\text{H}_2\text{O}} \text{B}
\]

would be:

A) \[
\text{CH}_3\text{CHCH}_3
\]

B) \[
\text{CH}_3\text{CDCH}_3
\]

C) \[
\text{CH}_3\text{CDCH}_3
\]

D) \[
\text{CH}_3\text{CHCH}_3
\]

E) \[
\text{CH}_3\text{CHCH}_2\text{D}
\]
19.10 Carbon Nucleophiles

- Recall the mechanism of the Grignard reaction is consistent with **basic conditions** (Grignards are strong nucleophiles/strong bases)

- Practice with Conceptual Checkpoint 19.30 – 19.31
19.10 Cyanohydrin Formation

- The cyanide ion is also a carbon-based nucleophile, and reversibly adds to ketones/aldehydes to form a cyanohydrin.

\[
\begin{align*}
\text{HCN} & \quad \text{HO} - \text{CN} \\
\text{A cyanohydrin} & \\
\end{align*}
\]

- This reaction works better under **basic conditions**, and so a catalytic amt of base is usually used.
19.10 Cyanohydrin Formation

• Mechanism of cyanohydrin formation under basic conditions:

Nucleophilic attack

The cyanide ion functions as a nucleophile and attacks the carbonyl group

Proton transfer

Protonation generates a cyanohydrin

• Acidic workup is not necessary since HCN serves as a source of protons
19.10 Cyanohydrin Formation

- To achieve basic conditions, KCN is usually added along with HCN.
- In this way, there is more CN\(^{-}\) than H\(^{+}\)

A new chiral center is possible in this reaction as well.
19.10 Cyanohydrin Formation

- Installation of a cyano group is advantageous because it can be converted to other functional groups:

![Chemical reaction diagram]

- Practice with Conceptual Checkpoint 19.32 – 19.33
19.11 Baeyer-Villiger Oxidation

- **Baeyer Villiger Oxidation** - An oxygen is inserted into an aldehyde/ketone between a carbonyl carbon and neighboring alkyl group.

\[
\text{RCO}_2\text{H} \rightarrow \text{RCO}_3\text{H} + \text{O}_2
\]

- **Mechanism:**

  The peroxycacid functions as a nucleophile and attacks the carbonyl group. A proton is transferred from one location to another, with simultaneous migration of an alkyl group. The carbonyl group is reformed, intramolecularly, because it would involve a five-membered transition state.

An aldehyde or ketone is converted to a carboxylic acid or ester, respectively.
Mechanism of reduction

H₃B-H

Ease of reduction
# Carbon (formal) oxidation states

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxidation State</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>+4</td>
</tr>
<tr>
<td>C-C(O)OH</td>
<td>+3</td>
</tr>
<tr>
<td>C-C(O)H</td>
<td>+1</td>
</tr>
<tr>
<td>C-CH$_2$-OH</td>
<td>-1</td>
</tr>
<tr>
<td>C-CH$_3$</td>
<td>-3</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>-4</td>
</tr>
</tbody>
</table>
From the qualitative point of view

**Oxidation**

Gaining O (increase ox state)

Loosing H

---

**Reduction**

Loosing O (decrease ox #)

Gaining H

---

\[
\begin{align*}
\text{RCH}_2\text{OH} & \rightarrow \text{RCH}_3 & \text{reduction} \\
\text{RCH}_2\text{OH} & \rightarrow \text{RC(O)OH} & \text{oxidation}
\end{align*}
\]
Aldehyde $\rightarrow$ alcohol

H$_2$  $\rightarrow$  Cr$_2$O$_7^{2-}$
LiAlH$_4$  $\rightarrow$  MnO$_4^-$
NaBH$_4$  $\rightarrow$  OsO$_4$

Ce$^{4+}$
19.12 Synthesis Strategies

- Should be able to make a list of products that can be made from aldehydes/ketones, and identify the reagents needed:

- Practice with SkillBuilder 19.7
19.13 Review of Reactions

1. H₂O₂ → [H⁺], H₂O
2. RO OR → [H⁺], ROH, -H₂O
3. Cyclohexene → [H⁺]
4. S-S → [H⁺]
5. Raney Ni
6. N-R
7. R-N-R
8. N-OH
9. N-NH₂
10. H₂ → NaOH, H₂O, heat
11. OH
12. OH
13. OH, CN
14. H₂C=PPh₃
15. RCO₂H